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ГЕОХИМИЧЕСКИЕ ХАРАКТЕРИСТИКИ И АНАЛИЗ ИСТОЧНИКОВ НЕФТИ В ГЛУБОКОВОДНОЙ ОБЛАСТИ БАЙЮНЬСКОЙ ВПАДИНЫ (*Южно-Китайское море*)

Дашуан Хэ[1,2,3], Дуцзе Хоу[1], Тао Чэнь[1]

[1]*School of Energy Resources, China University of Geosciences, Beijing, China 100083*
[2]*PRG, University of Calgary, Calgary, Alberta, Canada T2N 1N4*
[3]*PRG, University of Calgary, 2500 University Drive, NW Calgary, Alberta, T2N 1N4, Canad*

Источники нефти в Байюньской впадине до настоящего времени были мало изучены, что затрудняло определение нефтематеринских пород. Данная работа посвящена геохимическим исследованиям изотопов углерода, биомаркеров, обстановок осадконакопления и степени зрелости нефти из Байюньской впадины. Результаты исследований показывают, что органическое вещество нефти накапливалось в окислительной обстановке в условиях озерной фации и основным его источником являлись растения. Изученные образцы нефти характеризуются средней и высокой степенями зрелости. Нефть в северной части Байюньской впадины более зрелая, чем нефть в ее восточной части. Несмотря на ограниченное число данных по нефтематеринским породам, мы сделали вывод, что изученная нефть образовалась главным образом из пород эньпинской свиты. Другими возможными источниками нефти в разных областях впадины могли быть породы вэньчанской и чжухайской свит. Также были проанализированы источники нефти в каждой нефтеносной структуре Байюньской впадины; например, нефть в структуре LH19-5 образовалась из органического вещества эньпинской свиты, а нефть в структуре LW3-1 — из смешанного органического вещества эньпинской, вэньчанской и чжюхайской свит.

Глубинная вода, геохимические характеристики, источник нефти, Байюньская впадина.

GEOCHEMICAL CHARACTERISTICS AND ANALYSIS OF CRUDE-OIL SOURCE IN THE DEEP-WATER AREA OF THE BAIYUN SAG, SOUTH CHINA SEA

Dashuang He, Dujie Hou, and Tao Chen

In the Baiyun Sag, the oil relationship with possible source rocks is complicated, and little research on oil sources in the area has been performed. In this paper, geochemical studies of carbon isotopes, biomarkers, paleoenvironmental deposition, and crude oil maturity, carried out with the use of oil samples from the Baiyun Sag, demonstrate that the organic matter in crude oil has an oxidizing depositional environment and primarily lacustrine facies conditions, with a significantly higher plant input. The oil samples used are mature to highly mature. Crude oil in the northern area of the Baiyun Sag is more mature than samples in the eastern part of the sag. Despite limited source rock data, we were able to conclude that the crude oil samples were derived mainly from the Enping Formation; other potential source rocks of the Wenchang and Zhuhai Formations may also have contributed to the reservoirs in different parts of the sag. Furthermore, the source of crude oil in each structure in the Baiyun Sag was analyzed; for example, crude oil in the LH19-5 structure was generated from the organic matter of the Enping Formation, and crude oil in the LW3-1 structure was derived from the mixed organic matter of the Enping, Wenchang, and Zhuhai Formations.

Baiyun Sag, deep water, geochemical characteristics, oil source

INTRODUCTION

With an area of more than 2000 sq. km, the Baiyun Sag is a structural unit in the Zhu II depression in the Pearl River Mouth Basin. Most of the Baiyun Sag is located in the deep-water area of the South China Sea. A number of gas reservoirs associated with commercial light crude oil and condensate gas reservoirs have been found, thus indicating that the sag has good exploration and exploitation potential (He et al., 2012; Cui et al., 2009). Because hydrocarbon source rocks in the sag are buried to depths of about 4-5 km, correlating the oil to the source is difficult without access to corresponding source rock samples.

Biomarkers and carbon isotopes are considered as powerful tools in exploring petroleum geochemistry (Dawson et al., 2007; Maslen et al., 2011; Peters et al., 2005). Asif et al. (2011) previously studied oil-oil correlation and oil source through crude oil geochemical characteristics; and stable carbon and hydrogen isotopes. Biomarkers and carbon isotopes in bituminous organic matter can provide useful information about the source of their potential natural precursors and paleoenvironmental depositional conditions, as well as the thermal maturity of related source rocks (Asif et al., 2011; He et al., 2016). Furthermore, many of the abovementioned aspects are often related to and have been used for oil-source correlation or oil-oil correlation studies (Murray and Boreham, 1992). In many cases, crude oil found in a reservoir is most likely not sourced from a signal

✉e-mail: hds_0625@126.com
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source rock; instead, such oil usually has two or more sources. Therefore, efforts to correlate oil to source rock are full of uncertainty. Most of the crude oil varieties collected from the Baiyun Sag are characterized by multiple changes from multiple sources (He et al., 2012; Cui et al., 2009), so identifying their origins and possible migration pathways can be challenging. In this study, we seek to determine the source for different oil types from the Baiyun Sag through geochemical analyses of oil, including carbon isotopes and biomarkers, with limited source rock data. The study of crude oil geochemistry and oil-oil correlation increases the understanding of oil-source relationship, as well as petroleum migration pathways and accumulated processes in the Baiyun Sag.

GEOLOGICAL SETTINGS

The Baiyun Sag is located in the deep-water region of the Pearl River Mouth Basin, which is a Mesozoic-Cenozoic petroliferous basin in the northern South China Sea. The basin consists of five first-order tectonic units, which are as follows, from north to south: the northern step-fault zone, the northern depression zone, the central uplift zone, the southern depression zone, and the southern uplift zone. Each tectonic unit is divided into a number of sags and uplifts (He et al., 2012). The Baiyun Sag is a secondary tectonic unit in the southern depression zone within the Pearl River Mouth Basin. The stratigraphic succession in the Baiyun Sag is recognized in the following ascending order: Shenhu Formation (Fm) in the late Cretaceous, Wenchang Fm, Enping Fm, and Zhuhai Fm in Paleogene, Zhujiang Fm, Hanjiang Fm, Yuehai Fm, and Wanshang Fm in Neogene, and Quaternary.

The Baiyun Sag extends in the NEE-trending direction and has terrigenous input from the Pearl River. Thick hydrocarbon source rocks, primarily those of the Wenchang and Enping Fms, are well developed and buried to depths of 4-5 km. Previous geochemical studies carried out on the Baiyun Sag (Zhu et al., 2008; He et al., 2015) revealed that the Enping Fm is the primary source of hydrocarbons in the sag (He et al., 2016; Kim et al., 2013). Only a few wells intersected the Wenchang and Enping Fm; LW4-1-1 was the only well drilled to the bottom of the Wenchang Fm, while the PY33-1-1 and PY27-2-1 wells reached the bottom of the Enping Fm (Guo et al., 2008; Zhu et al., 2008).

MATERIALS AND METHODS

The locations of the structures from which the crude oil samples herein were collected are shown in Figure 1. All Twenty-four (24) samples used in this study were selected from the Oligocene Zhujiang Fm and all of them are crude oils, whereas rock samples of source rocks could not be obtained. The oil sample (10 ml) was

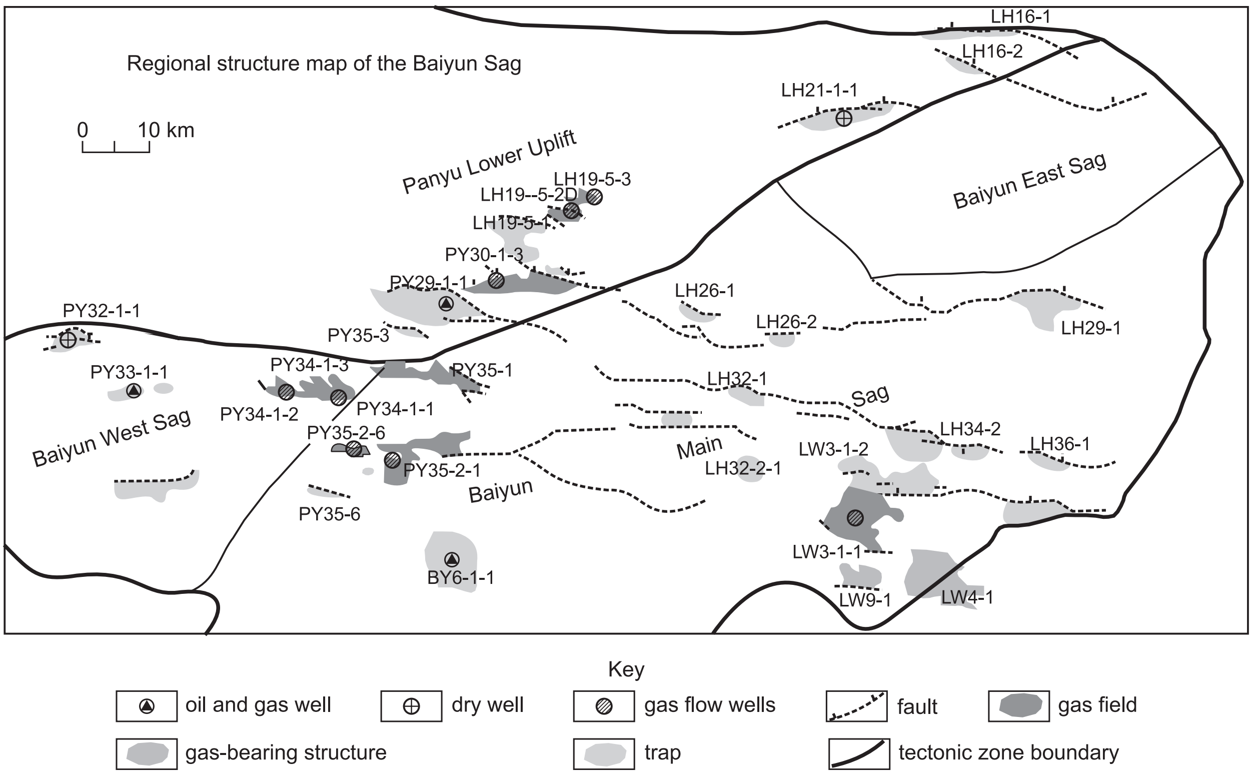


Fig. 1. Map of the Baiyun Sag showing the regional structure and location of sampled crude oil wells.

mixed with pentane (50 ml) and the mixture was filtered to remove the asphaltenes. Then the extracts were fractionated by column chromatography on alumina over silica gel. The columns were washed successively with 50 ml volumes of hexane, toluene and methanol to elute the aliphatic, aromatic and non-polar fractions, respectively. The aliphatic and aromatic fractions were concentrated to the volume of less than 1 ml using a stream of filtered nitrogen gas, and then the extract was adjusted to 1 mL exactly and transferred to a GC-MS vial. Each vial of extract was subjected to gas chromatography-mass spectrometry (GC-MS) analysis.

GC-MS (Agilent Technologies Company) was conducted at the Key Laboratory Testing Center of the Marine Reservoir Evolution and Petroleum Accumulation Mechanism at China University of Geosciences, Beijing. The analytical conditions of GC-MS were as follows: carrier gas, 99.999% helium; injector temperature, 300°C; chromatographic column, VF-5MS (60 m×0.25 mm×0.25 μm); column temperature, initial temperature of 50°C, 20°C / min up to 120°C, maintain 1 min, 3°C / min up to 310°C, maintain 25 min; carrier gas flow rate, 1 ml/min constant; split injection, 1 uL, split ratio 5:1; mass spectrometer conditions: Electron ionization, 70ev; data acquisition mode, selected ion monitoring (SIM).

Furthermore, carbon isotope analyses of 16 crude oil samples were conducted at the Geochemical Experimental Center at the Geological Research Institute of the Shengli Oilfield in China. Oil carbon isotope experiments were performed using a MAT 252 isotope ratio mass spectrometer (Finngan MAT 252, Germany). Determinations of $\delta^{13}C$ values of crude oil were made using standard, sealed-tube combustion techniques, with CuO serving as the O_2 donor. Carbon dioxide was used as working reference gases. All results are reported in parts per thousand (‰) relative to the PeeDee Belemnite (PDB) standard.

RESULTS AND DISCUSSION

Normal alkanes and regular isoprenoid distributions. The total ion chromatogram (TIC) of a representative oil sample (well LH34-2-1/2987 m) is shown in Figure 2. *n*-Alkanes ranging from C_{10}-C_{35} and isoprenoids are observed, but *n*-alkanes less than C_{10} are not, possibly due to evaporative loss during the sampling process. Pr/Ph ratios and some isoprenoid parameters are calculated from the TIC. All of the samples are found to have Pr/Ph ratios ranging from 2.87 to 5.90, thus indicating an oxidizing type of sedimentary environment (Koopmans et al., 1999). The Pr/Ph ratio of crude oil ranges from 3.91 to 5.90 in the northern Panyu Lower Uplift and from 2.87 to 4.32 in the eastern Liuhua-Liwan Structure Belt. Oil varieties from the northern district have a higher Pr/Ph ratio compared to those from the eastern area, which suggests that the source rocks for these oils were deposited in completely oxidizing environments (Hughes et al., 1995; He et al., 2015). Representative TIC of the saturated fraction (Fig. 2) shows the presence of a full suite of *n*-alkanes and the absence of unresolved complex mixtures (UCM), suggesting that no biodegradation has occurred (Koopmans et al., 1999).

According to the isoprenoid parameters of Pr/*n*-C_{17} and Ph/*n*-C_{18} (Fig. 3) (Hughes et al., 1995), the parent material of crude oil in the Baiyun Sag is mainly humus generated from terrigenous organic materials in an oxidizing environment. Isoprenoids show resistance to biodegradation compared with *n*-alkanes; thus, the isoprenoids/*n*-alkanes ratio is higher in biodegraded oils (Peters et al., 2005). However, in the present case, the

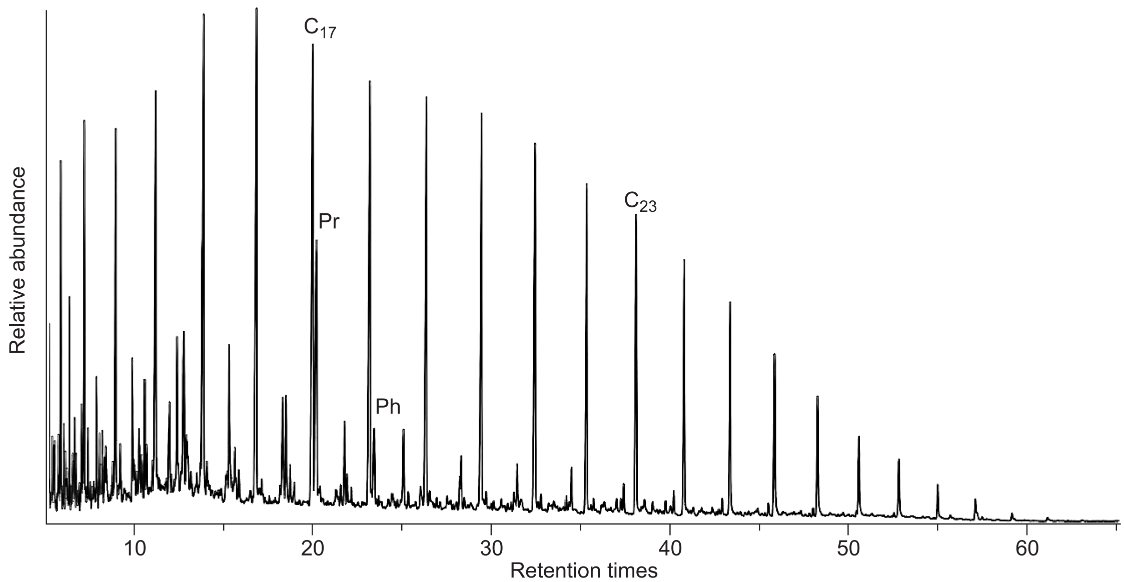


Fig. 2. Representative TIC of saturated hydrocarbons of the crude oil (well LH34-2-1/2987 m) in the Baiyun Sag.

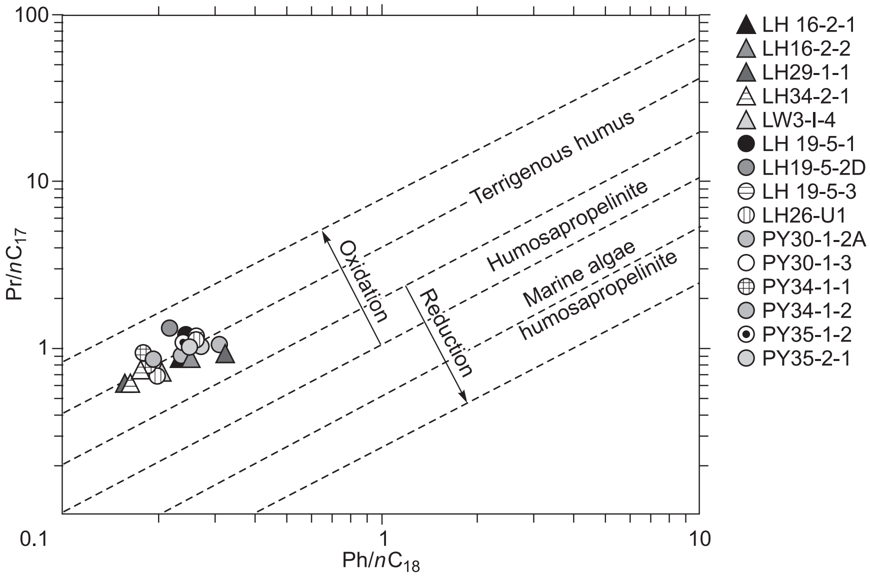


Fig. 3. Plot of isoprenoid parameters of Pr/nC17 and Ph/nC18,with logarithmic coordinates.

Pr/n-C_{17} and Ph/n-C_{18} ratios of the sampled oils are 0.55-1.20 and 0.15-0.32, respectively. A relatively higher concentration of n-C_{17} and n-C_{18} alkanes compared with pristane and phytane, together with no detection of UCM, suggesting that the oils are pristine and that no biodegradation has occurred (Koopmans et al., 1999).

Carbon isotope distributions. The sixteen crude oil samples from the Baiyun Sag are characterized by a $\delta^{13}C$ that ranges from -26.3‰ to -28.0‰ (Fig. 4). Generally, oils of lacustrine origin have a less negative $\delta^{13}C$ value (i.e., are isotopically heavier), with a maximum value of more than -30‰; meanwhile, marine genetic oil has a more negative $\delta^{13}C$ (i.e., is isotopically lighter), which is less than -30‰ (Schoell et al., 1984; Hughes et al., 1995; Gladkochub et al., 2013). In the present case, $\delta^{13}C$ in crude oils are relatively heavier (more than -30‰), indicating that the oil samples are derived from terrigenous organic matter deposited in the lacustrine sedimentary environment (Peters et al., 2005; Requejo et al., 1996; Yan et al., 2014).

Oils from the LH19-5 structure (including well LH19-5-1/2511.5 m; LH19-5-2D/2136 m; LH19-5-3/2473m), well PY35-1-2, and well PY35-2-1 have a relatively lighter $\delta^{13}C$ that varies from -27.3‰ to -28.0‰. Meanwhile, oils from well PY34-1-1, PY34-1-2(3364 m), PY35-1-2, and the LW 3-1 structure (including well LW3-1-2/3070 m, LW3-1-3/3140 m and LW3-1-4/3163 m) display a heavier $\delta^{13}C$ of about -26.3‰. Other oil samples have intermediate $\delta^{13}C$ values near -27.0‰. The difference in $\delta^{13}C$ of crude oils likely represents source variations and various depositional environments, as well as differences in maturity (Gladkochub et al.,

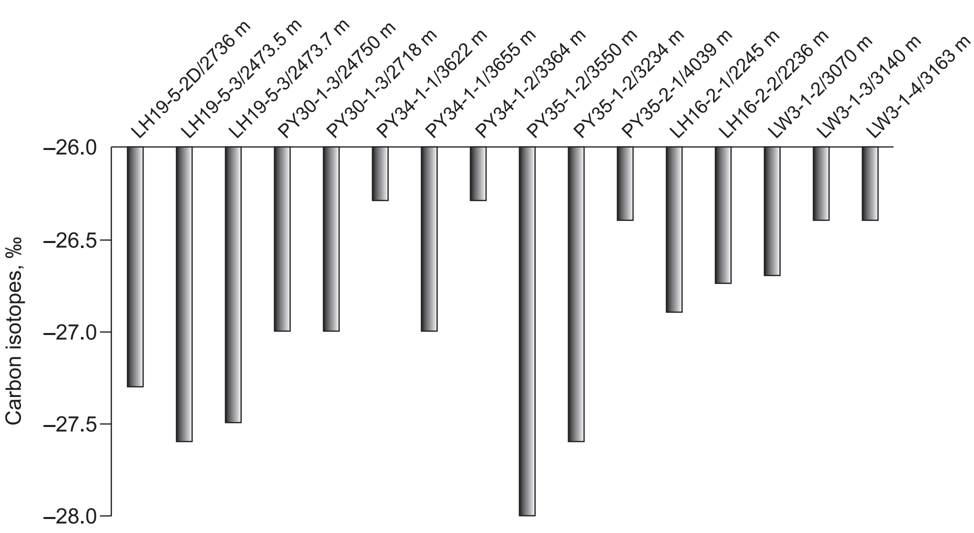
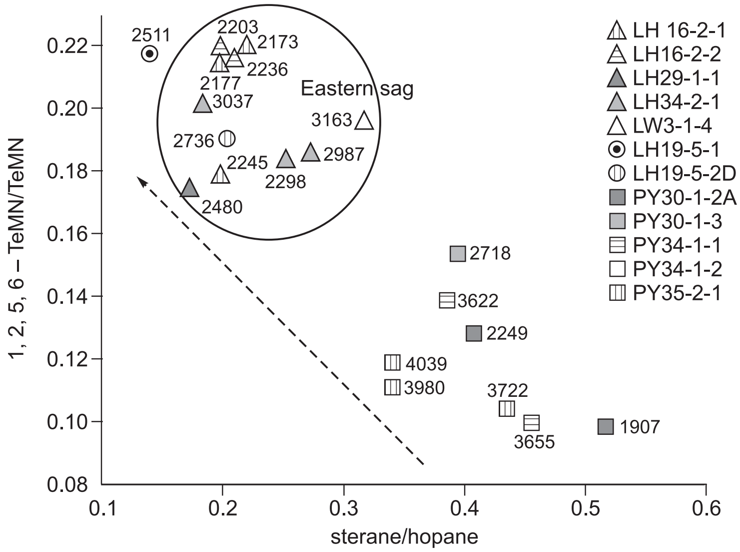


Fig. 4. Distributions of carbon isotope of oil samples in the Baiyun Sag.

Fig. 5. Correlation of sterane/ hopane and 1,2,5,6-TeMN/TeMN of crude oils. The number besides the point indicates depth (m), the same below.



2013; Strakhovenko et al., 2014). We will discuss the causes for $\delta^{13}C$ differences and their relation to oil sources in the following sections.

Biological source and sedimentary environment. Minor amounts of oleanane and bicadinanes were detected in the oil samples, indicating that organic matter in the Baiyun Sag originated from terrigenous higher plants (Alberdi and López, 2000; Zhu et al., 2008). A low content of tricyclic terpanes, dominated by C_{19} tricyclic terpane, is observed in oil samples, while a high content of hopanes is demonstrated, with the exception of gammacerane. Both the dominance of C_{29} steranes and the detection of terrigenous triterpanes indicate the input of terrigenous plants (Peters et al., 2005), coinciding with the results of the carbon isotopes. Some of the other samples reveal C_{27}-C_{29} sterane equipollence. The aromatic hydrocarbons mainly consist of naphthalene, biphenyl, phenanthrene, and trifluorene series, which account for about 90% of the total aromatic hydrocarbons, while minor amounts of benzo-fluoranthene, fluoranthene, pyrene, and triaromatic steroids are detected (He et al., 2015), further supporting the presence of terrigenous higher plant input (Petrova et al., 2010; Jia et al., 2009).

A DBT/P ratio less than 0.26 demonstrates that the organic matter in crude oil is derived from terrigenous plants deposited in an oxidizing environment (Hughes et al., 1995; Berthou and Vignier, 1986). The sterane/hopane ratio is lower than 0.52 (Fig. 5), which also indicates terrigenous organic matter input (Moldowan et al., 1985; Kashirtsev et al., 2009, 2013). Oil samples taken from the eastern sag have higher ratios of 1,2,5,6-TeMN/TeMN (TeMN refers to tetramethyl naphthalene, TeMN group herein includes twelve tetramethyl naphthalene compounds) and OL/C_{30} (oleanane/C_{30} hopane) but a lower ratio of sterane/hopane compared to the oil samples taken from the northern sag (Fig. 5 and 6). This finding suggests that the organic matter in the eastern sag has a higher degree of terrigenous plant input than in the northern area.

Crude oil maturity. Some previous studies have proposed that many biomarker parameters reach equilibrium of the oil-generation window and thus may not be useful for highly mature oils or condensates (Chakhmakhchev et al., 1997; Van Graas, 1990; Li and Lin, 2006). Among the oil samples studied, the rearranged sterane -regular sterane ratio varies from 2.0 to 8.2, and the sterane maturity parameters of C_{29} 20S/(20S+20R) and C_{29} ββ/(αα+ββ) range from 0.38 to 0.57 and 0.40 to 0.62, respectively, indicating that isomerization equilibrium (Van Graas, 1990; Strakhovenko et al., 2014) has been reached. Therefore, these parameters are unreliable. In this study, cycloalkanes of adamantane may be more effective in evaluating oil maturity. The adamantane parameter (MDI = = 4-MD/4-MD + 3-MD +1-MD, MD refers to methyl double adamantane) can be correlated with vitrinite reflectance Ro, that is Ro = 0.2846 + 0.0312 MDI (Wingert, 1992; Kashirtsev et al., 2013; Petrova et al., 2010). According to this equation, Ro is found to be between 1.27% and

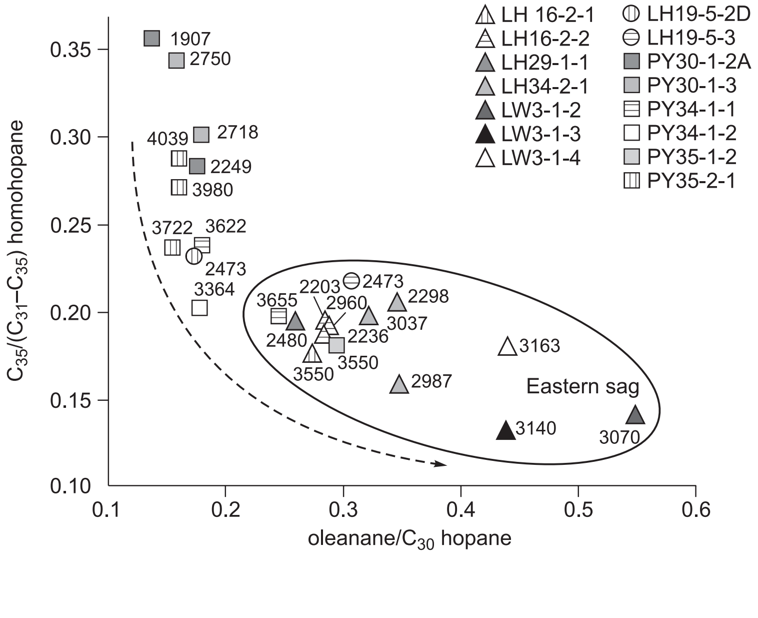


Fig. 6. Correlation of oleanane/C_{30} hopane and C_{35}/ (C_{31}–C_{35}) homohopane of crude oils.

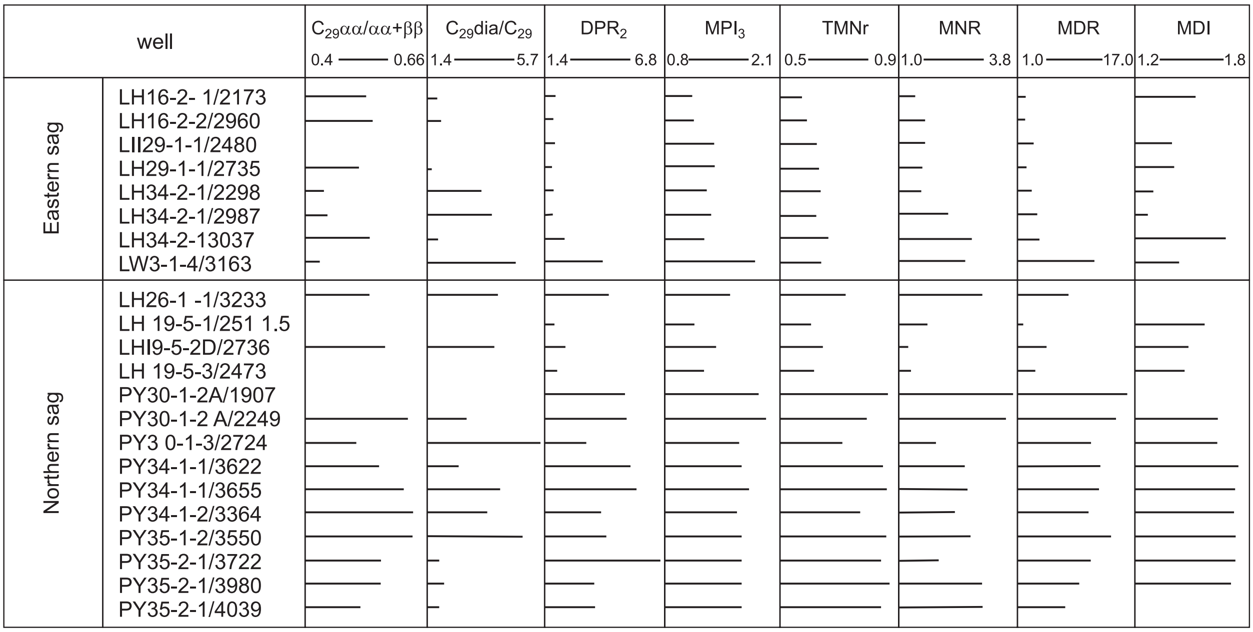


Fig. 7. Summary of maturity parameters in crude oils in the Baiyun Sag.

Note: C_{29} αα/(αα + ββ) = C_{29} sterane αα/(αα + ββ), C_{29} dia/C_{29} = rearranged and regular sterane ratio, DPR_2 = 2,7-DMP/1,8-DMP, MPI_3 = = (3-MP + 2-MP)/(9-MP + 1-MP), TMNr = 2,3,6-TMN/(1,2,5-TMN + 2,3,6-TMN), MNR = 2-MN/1-MN, MDR = 4-MDBT/1-MDBT, MDI = 4-MD/(4-MD + 3-MD + 1-MD).

1.74%, indicating that the crude oil samples are condensate oil or light oil generated in a high maturity stage. The other aromatic parameter of the trimethyl naphthalene ratio (TMNr=2,3,6-TMN/(2,3,6-TMN+ 1,2,5-TMN) (Radke et al., 1986) ranged from 0.5 to 0.9, thus further showing that the crude oil is of high maturity (Alexander et al., 1995).

With respect to other maturity parameters of MPI3, MDR and MNR (MPI3 = (3-MP + 2-MP)/(9-MP + 1-MP), MDR = 4-MDBT/1-MDBT, MNR= 2-MN/1-MN, MP- methyl phenanthrene, MDBT-methyl dibenzothiophene, MN-methyl naphthalene) (Radke et al, 1986; Alexander et al., 1995), both of them show the significant maturity difference among the crude oils from the eastern and northern areas. MPI3, MDR and MNR ratios of crude oils in the eastern sag range among 0.89-1.16, 1.72-5.07 and 1.32-2.71, respectively; whereas these maturity parameters distribute among 1.36-2.09, 8.47-16.01 and 1.76-3.64, respectively in the crude oils from the northern sag. In general, oils in the northern sag have higher maturity compared with those in the eastern sag, with the exception of the oils in the LH19-5 structure and well LW3-1-4 which have MPI3, MDR and MNR ratios of 0.91-1.18, 3.04-5.97, 1.12-1.60 and 1.84, 11.87, 2.51, respectively.

Our summary of oil maturity parameters (Fig. 7) displays a significant maturity difference based on a regional scale; crude oils in the northern sag are more mature than oils in the eastern sag. However, oil from well LW3-1-4 located in the eastern sag shows intermediate maturity between the eastern and northern sags. Oils from the LH19-5 structure in the northern sag have a relatively lower maturity compared to northern oil samples, which may be caused by its derivation from a different source than the other oil samples in the northern sag.

Source of crude oils. A summary of the geochemical characteristics of source rocks in the Baiyun Sag is proposed based on the source rock data collected from previously published studies (Cui et al., 2009; Zhu et al., 2008; Guo et al., 2008; He et al., 2012), as well as internal data from the Shenzhen Branch of CNOOC in Guangzhou, China. The collected source rock data are summarized as follows: 1). Wenchang Fm (well LW4-1-1): the Pr/Ph ratio is 1.42-1.62; shallow lake–semideep lake facies sediments in a reducing environment, it shows C_{27} sterane dominance, a low content of 4-methyl steroids, terrigenous tricyclic terpanes, bicadinanes (resins) and oleananes; the organic matter is rich in amorphous and planktonic algae of the sapropelic type; it has a higher hydrocarbon generation potential (8.18-13.64 mg/g); and it shows a higher hydrogen index, ranging from 446 to 566 mg/g TOC, highly mature to over mature. 2). Enping Fm (well PY33-1-1): the Pr/Ph ratio is from 1.44 to 5.87, fresh water-lacustrine facies sediments in an oxidizing–weakly oxidizing environment, it shows low 4-methyl steroids, C_{29} sterane dominance, abundant terrigenous tricyclic terpanes and bicadinanes, and low-moderate oleanane, it is terrigenous sourced organic matter of the humic type; and it displays higher hydrocarbon generation potential (0.56-97.47 mg/g) with a low to moderate hydrogen index, ranging from 50 to 300 mg/g TOC, highly mature. 3). Zhuhai Fm: the Pr/Ph ratio is from 2.47 to 5.29, transitional facies sediments that are greatly affected by terrestrial organic matter; its C_{27} and C_{29} steranes are nearly equal, it shows low 4-methyl steroids; and it is abundant in terrigenous tricyclic terpanes and oleananes, but poor in bicadinanes (W, T); it displays moderate hydrocarbon generation potential (0.99-4.20 mg/g) with a lower hydrogen index of 128-265 mg/g TOC, and its organic matter is humic and in the mature stage.

In this study, the geochemical characteristics of crude oil collected from the Baiyun Sag are summarized as follows: the Pr/Ph ratio ranges from 2.87 to 5.90, it contains abundant terrigenous tricyclic terpanes, minor amounts of oleananes and bicadinanes, a low content of 4-methyl steroids, and a lower sterane/hopane ratio with a higher ratio of C_{19}/C_{23} tricyclic terpanes; it shows C_{29} steranes dominance or nearly equal C_{27} and C_{29} steranes; and most of the crude oils are highly mature. Together with the summarized geochemical characteristics of source rocks, the Enping Fm is assumed to be the location of the primary source rocks for crude oil production. Nevertheless, determining whether the oil has a single source or mixed source, as well as evaluating the hydrocarbon contribution of each formation in an individual structure, is still difficult. In the following section, the source beds of crude oil in each structure are discussed.

The $\delta^{13}C$ of crude oil is easily influenced by various factors, including sedimentary environment, biological source, maturity, and secondary alteration, etc. (Hughes et al., 1995; Huang and Pearson, 1999). In the correlation plots of $\delta^{13}C$ and some biomarker ratios that provide information regarding the origin of oil and its sedimentary environment (Fig. 8), oil samples from well PY34-1-1, PY34-1-2, PY35-2-1, LW3-1-3, and LW3-1-4 display a heavier $\delta^{13}C$, lower tricyclic terpane/hopane, C_{29}/C_{27} rearranged sterane and DBT/P (DBT= Dibenzothiophene, P=Phenanthrene) ratios, and a higher sterane/hopane ratio. Both of these ratio parameters reflect organic matter related to the Wenchang Fm (Berthou and Vignier, 1986; kashirtsev et al., 2009; Hughes et al., 1995). That is, crude oils with heavier $\delta^{13}C$ are correlated with the Wenchang Fm. Similarly, oils from well LH16-2-1 and LH16-2-2 have moderate $\delta^{13}C$ (Fig. 8), while they display lower tricyclic terpane and hopane

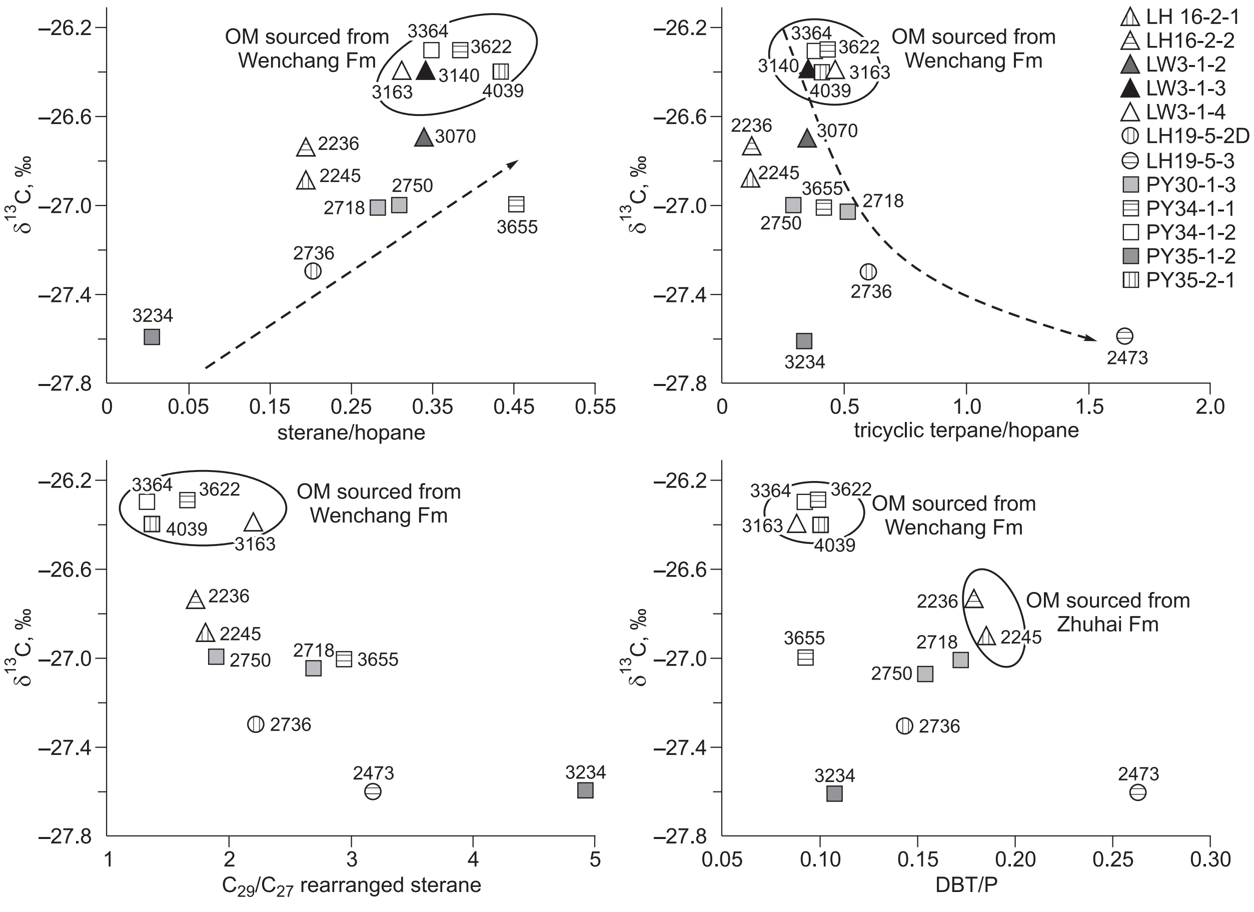


Fig. 8. Correlation plots of carbon isotopes and source and sedimentary environmental parameters of crude oils in the Baiyun Sag.

Note: OM refers to organic matter, Fm refers to formation, the same below.

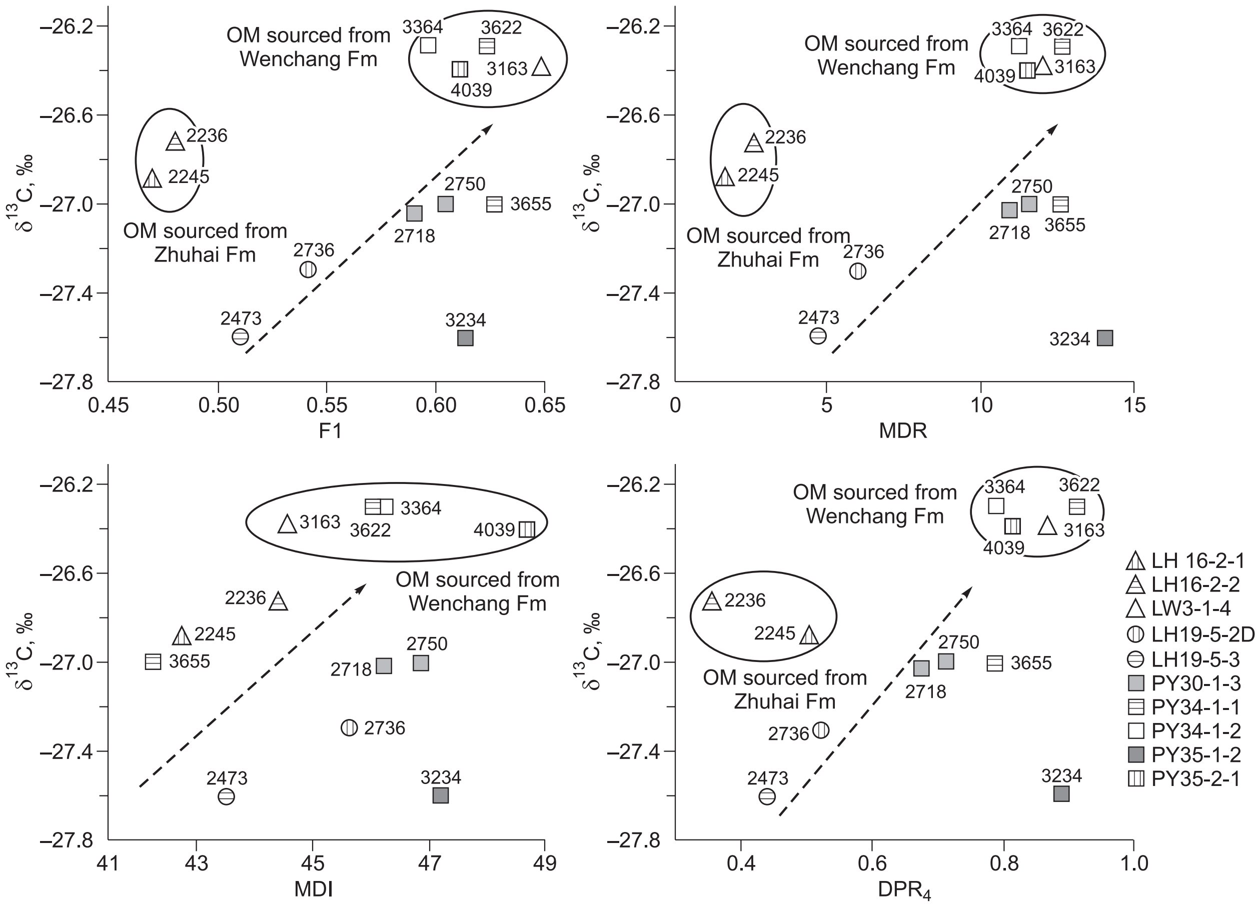


Fig. 9. Correlation plots of carbon isotopes and maturity parameters of crude oils in the Baiyun Sag.

Note: F1 = (3-MP + 2-MP)/(1-MP + 9-MP + 3-MP+2-MP); MDR = 4-MDBT/1-MDBT, MDI = 4-MD/(4-MD + 3-MD + 1-MD); DPR4 = = 2,7-DMP/1,7-DMP.

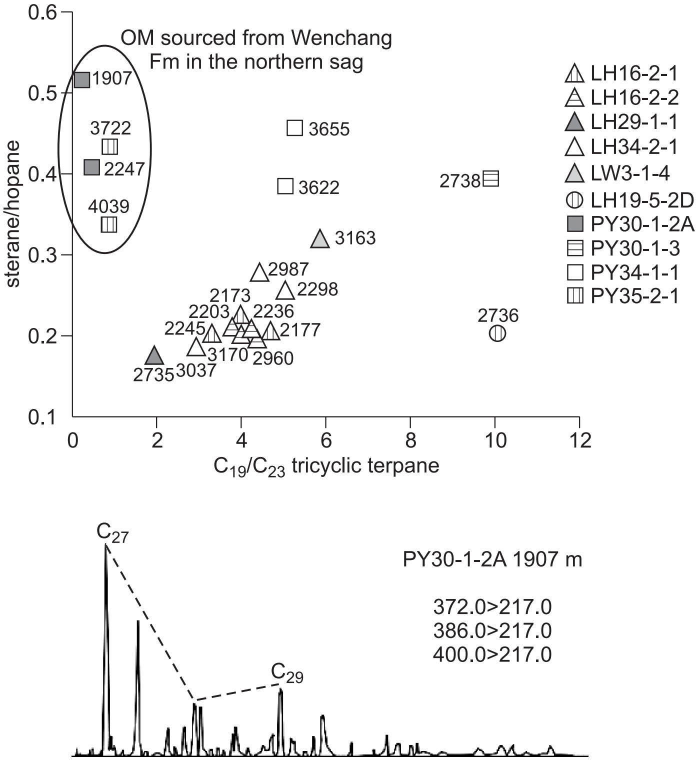
ratios, higher DBT/P, and intermediate C_{29}/C_{27} rearranged sterane ratios. These biomarkers reflect that the crude oils in the LH16-2 structure (including crude oils from well LH16-2-1 and LH16-2-2) are correlated with the Zhuhai Fm.

The correlation plots of oil carbon isotope and maturity parameters (Fig. 9) show that highly mature crude oils in the northern sag, such as oils from well PY34-1-1, PY34-1-2, PY35-2-1, and LW3-1-4, have heavier $\delta^{13}C$. Generally, the $\delta^{13}C$ value of oil increases as its maturity increases (Radke et al., 1986; Kim et al., 2013). Source rocks in the Wenchang Fm have reached a high maturity stage; therefore, mixed oils originated from the Enping and Wenchang Fms may have a heavier $\delta^{13}C$ and higher maturity compared to oil sourced from the Enping Fm alone. Furthermore, crude oil from well PY30-2-1A and PY35-2-1 in the northern sag are characterized by a lower C_{19}/C_{23} tricyclic terpane ratio, a higher sterane/hopane ratio, and a low abundance of oleananes and bicadinanes, as well as abundant C_{27} sterane and high oil maturity (Fig. 10), these characteristics are corresponded to the Wenchang Fm (He et al., 2016; Zhu et al., 2008). Therefore, the Wenchang Fm is the main source bed of oils from well PY30-2-1A and PY35-2-1.

Oil types from well LH16-2-1 or well LH16-2-2 show relatively lower maturity and heavier $\delta^{13}C$ values. The lower maturity could be attributed to the mixed sources from the Zhuhai and Enping Fms because source rock in the Zhuhai Fm has lower maturity. However, low mature oils should have a lighter $\delta^{13}C$, which contradicts the moderate $\delta^{13}C$ values observed. Other factors may have influenced the $\delta^{13}C$ value of crude oil in the LH16-2 structure.

Moldowan (1985) proposed that the presence of C_{30} sterane in crude oil is powerful evidence that indicates marine organic matter input in the source rock. In our study, C_{30} steranes were detected in the oils from well LH16-2-1, LH16-2-2, LH29-1-1, and LH34-2-1 in the eastern sag, which highly correlates with the Zhuhai Fm deposited in the marine or transitional facies. The $\delta^{13}C$ value could be influenced by depositional condi-

Fig. 10. Correlation plot of C_{19}/C_{23} tricyclic terpane and sterane/hopane and mass chromatogram of C_{27}-C_{29} steranes of crude oils in the Baiyun Sag.



tions, and organic matter deposited in the marine environment has a heavier $\delta^{13}C$ value than that in the terrestrial facies (Schoell et al., 1984; Hughes et al., 1995), which could increase the $\delta^{13}C$ value of oils in the eastern sag. Furthermore, oils with low maturity have a lower ratio of saturates/aromatics and non-hydrocarbon/asphaltene compared with mature or highly mature oils (Peters et al., 2005). In our study, significantly higher ratios of saturate/aromatic and non-hydrocarbon/asphaltene are displayed in the oils in the eastern sag (Fig. 11), further supporting that the oils in the eastern sag have a lower maturity than the oils in the northern sag.

The Enping Fm is the primary source rock in the Baiyun Sag. The correlation plots of Figure 8-11 show that the oils in well PY30-1-2A, PY35-2-1, and PY34-1-1 from the northern sag have organic matter derived from the Wenchang Fm, while oils from the LH16-2 structure and well LH34-2-1 and LH29-1-1 have organic matter derived from the Zhuhai Fm. Oil varieties in well PY30-1-2A, PY34-1-1, and PY35-2-1 (S2-WC) in the northern sag have higher $\delta^{13}C$ values, ranging from -27.0‰ to -26.3‰, an intermediate C_{19}/C_{23} tricyclic terpane ratio of 0.87-5.84, a higher sterane/hopane ratio of 0.34-0.46, low abundance of oleananes and bicadinanes, C_{27} sterane dominance in steranes (Fig. 10), and high maturity (Ro=1.70%-1.74%). These characteristics correspond with the Wenchang Fm (He et al., 2016; Zhu et al., 2008). Therefore, the Wenchang Fm is the main source bed for well PY30-1-2A, PY34-1-1, and PY35-2-1. In the eastern sag, oil varieties in the LH16-2 structure and well LH34-2-1 and LH29-1-1 (M2) are characterized by higher $\delta^{13}C$ values ranging from -26.7‰ to -26.9‰, lower bicadinanes but higher oleananes, a lower sterane/hopane ratio and C_{19}/C_{23} tricyclic terpane ratio of 0.17-0.25 and 1.97-5.03, respectively, and relatively lower oil maturity ranging from 1.27-1.51, indicating that their oil source could be from the Enping and Zhuhai Fms. Moreover, we also studied oil sources in other structures based on $\delta^{13}C$ values, biomarkers and limited source rock data. For example, oils in the LH19-5 structure (S1-EP) have a light $\delta^{13}C$ of -27.6‰ to -27.3‰, medium to high maturity (Ro=1.43%-1.50%), C_{29} sterane dominance, abundant tricyclic terpanes, medium oleanane content, and a higher C_{19}/C_{23} tricyclic terpanes ratio of 8.82-10.05. These characteristics coincide with the source rocks in the Enping Fm. From a geological perspective, a stratigraphic gap exists in the bottom of the northern LH19-5 structure where the

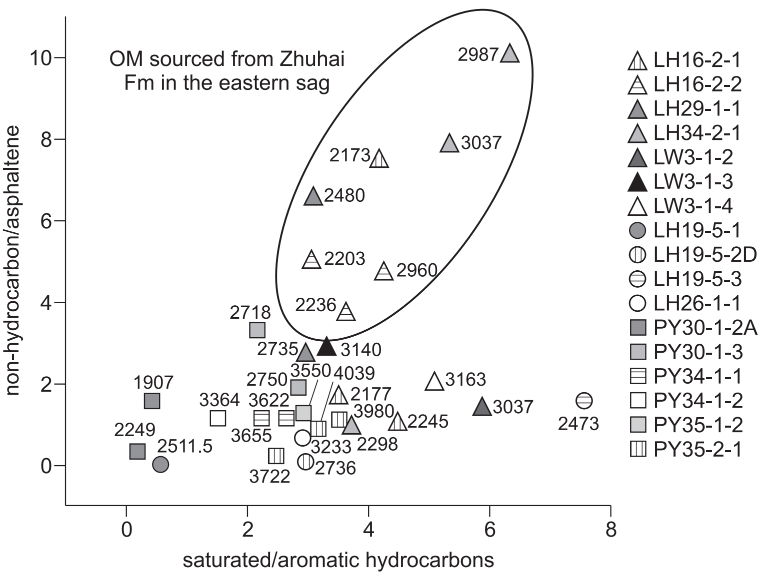


Fig. 11. Correlation of saturated/aromatic hydrocarbons and non-hydrocarbon/asphaltene of crude oils in the Baiyun Sag.

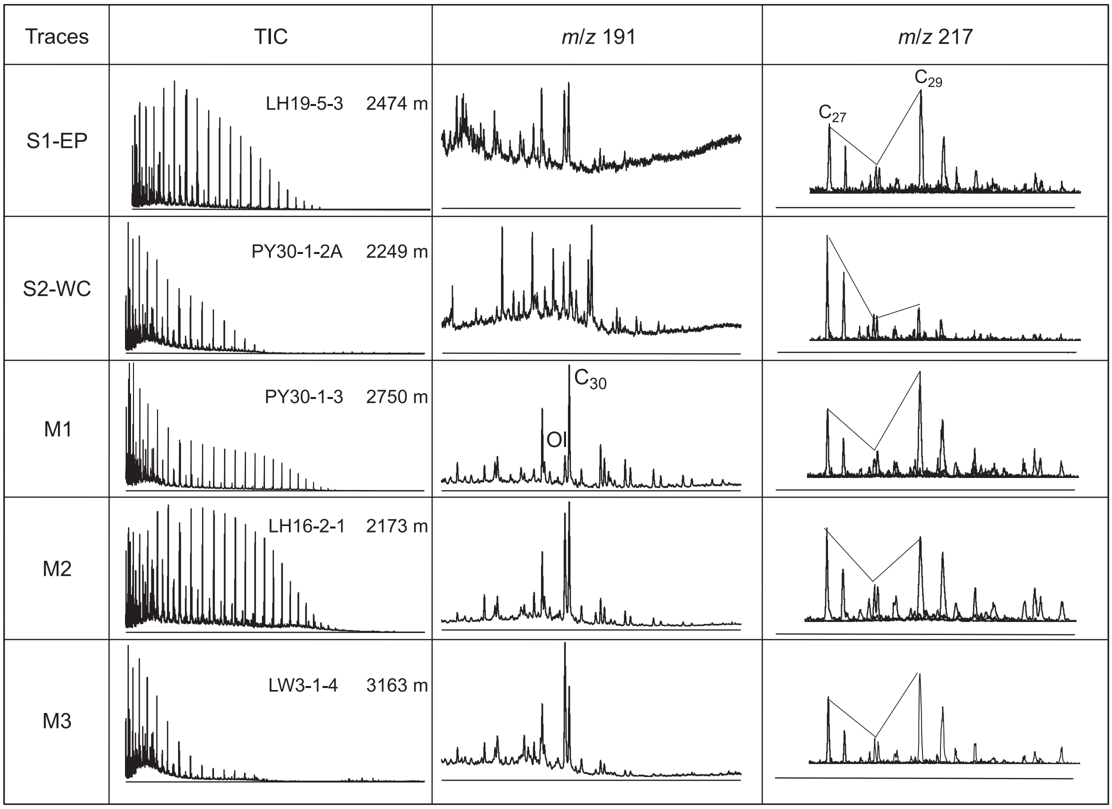


Fig. 12. GC-MS TIC, *m/z* 191 and m/z 217 traces of five oil samples representing different sources.

Wenchang Fm is missing because of tectonic movement (He et al., 2012; Petrova et al., 2010). A great deep fault cuts through to the Enping Fm, which is the source bed; therefore, the Enping Fm is considered as the primary source bed for generating hydrocarbons in the LH19-5 structure. Oils in well PY30-1-3, PY35-1-2, and LH26-1-1 (M1) are characterized by higher $\delta^{13}C$ values ranging from -26.7‰ to -26.0‰, fewer bicadinanes and less medium oleanane, a higher C_{19}/C_{23} tricyclic terpane ratio of 5.48-9.92, an intermediate sterane/hopane ratio of 0.22-0.39, C_{29} steranes dominance, and higher Ro maturity, ranging from 1.63 to 1.69, suggesting that their oil may possibly have mixed sources from the Enping and Wenchang Fms. Lastly, oils in the LW3-1 structure (M3) have relatively higher $\delta^{13}C$ values, ranging from -27.1‰ to -26.4‰; abundant oleanane and tricyclic terpanes, a higher C_{29} sterane content, and their maturities (Ro=1.40%-1.43%) are intermediate between the northern and eastern sags (Fig. 7), suggesting that they may be related to either the Wenchang Fm or the Zhuhai Fm. The regional distribution of alkyl naphthalene, alkyl biphenyl, and alkyl phenanthrene in the LW3-1 structure is also intermediate between the northern and eastern areas (He et al., 2016; Kuibida et al., 2014). This structure is located in the south of the main sag, as well in the southwest of the eastern sag, so crude oil in the LW3-1 structure can be assumed to be mixed oil from the Enping, Wenchang, and Zhuhai Fms.

TIC and mass chromatograms (m/z 191, m/z 217) of five samples with different sources are presented in Fig. 12. The total ion chromatograms of the five oil samples are inconsistent with each other, and the high molecular weight compounds in S2-WC and M3 are less abundant than in the other three, most likely due to the high maturity of source beds in the Wenchang Fm. These five oil samples have a different abundance of oleanane and C_{30} hopane in *m/z* 191 trace, representing their different parental materials. Oils derived from the Enping and Zhuhai Fms have a higher content of oleanane than those derived from the Wenchang Fm. Apparently, the content of oleanane in M2 and M3 is higher than the others, that their oleanane/C_{30} hopane ratio is between 0.79-1.23 and 1.69-2.25, respectively. In *m/z* 217 trace, oils display different sterane distributions, primarily C_{27}, $C_{28,}$ and C_{29} steranes. For example, C_{29} sterane in S1-EP, M1, and M3 is more abundant than C_{27}, while in S2-WC, the content of C_{27} sterane is higher than $C_{29,}$ such that the ratio of C_{27}/C_{29} sterane can reach 3.01. The oil in M2, which is sourced from Enping and Zhuahi Fms, has a slightly higher content of C_{29} than C_{27} steranes or $C_{29,}$ and C_{27} steranes are approximately equal, such that the ratio of C_{27}/C_{29} sterane ranges from 0.43-1.09.

The geochemical characteristics of crude oil in relation to the source rocks are shown in Table 1. In the northern sag, crude oils in the LH19-5 structure come from the Enping Fm; crude oils in the PY34-1 and PY35-

Geochemical characteristics of crude oil varieties related to their source rocks in the Baiyun Sag

Source of oil	Geochemical biomarkers						
	$\delta^{13}C$ (‰)	Maturity (Ro–Ad, %)	Bicadinanes/ C_{30} hopane	Oleanane/ C_{30} hopane	C_{27}/C_{29} Sterane	C_{19}/C_{23} tricylic terpane	Sterane/ hopane
S1–EP	–27.6~ –27.3	1.43–1.50	0.065–0.14	0.37–1.03	0.31–0.51	8.82–10.05	0.14–0.20
S2–WC	–27.0~ –26.3	1.70–1.74	0.004–0.082	0.28–0.73	0.90–3.01	0.87–5.48	0.34–0.52
M1	–26.7~ –26.0	1.63–1.69	0–0.096	0.23–0.39	0.24–0.75	5.48–9.92	0.22–0.39
M2	–26.9~ –26.7	1.27–1.51	0.023–0.052	0.79–1.23	0.63–1.09	1.97–5.03	0.17–0.25
M3	–27.1~ –26.4	1.40–1.43	0.043–0.066	1.69–2.25	0.39–0.46	4.3–5.89	0.32–0.34

Note: S1–EP: single source from the Enping Fm; S1–WC: single source from the Wenchang Fm; M1: mixed sources from the Enping and Wenchang Fm; M2: mixed sources from the Enping and Zhuhai Fms; M3: mixed sources from the Enping, Wenchang and Zhuhai Fms. Ro– vitrinite reflectance, Ad– adamantine.

2 structures come from the Wenchang Fm; crude oils in the PY35-1 structure and well PY30-1-3 and LH26-1-1 have a mixed source, and the Enping and Wenchang Fms are the source rocks that supplied the hydrocarbons. In the eastern sag, crude oils in the LH16-2, LH29-1, and LH34-2 structures have a mixed source from the Enping and Zhuhai Fms; crude oils in the LW3-1 structure are also mixed source oil from the Enping, Wenchang, and Zhuhai Fms. The surface distribution of oil source in the Baiyun Sag is shown in Figure 13.

Interestingly, well PY30-1-3 and well PY30-1-2A were both drilled in the same geological structure, but they have different oil sources (Fig. 12). Crude oils in well PY30-1-2A are from the Wenchang Fm. In the PY30-1 structure, a great deep fault cuts through the bottom of the Wenchang Fm, and the fault is in close proximity to well PY30-1-2A; therefore, oil generated from the Wenchang Fm migrated vertically along frac-

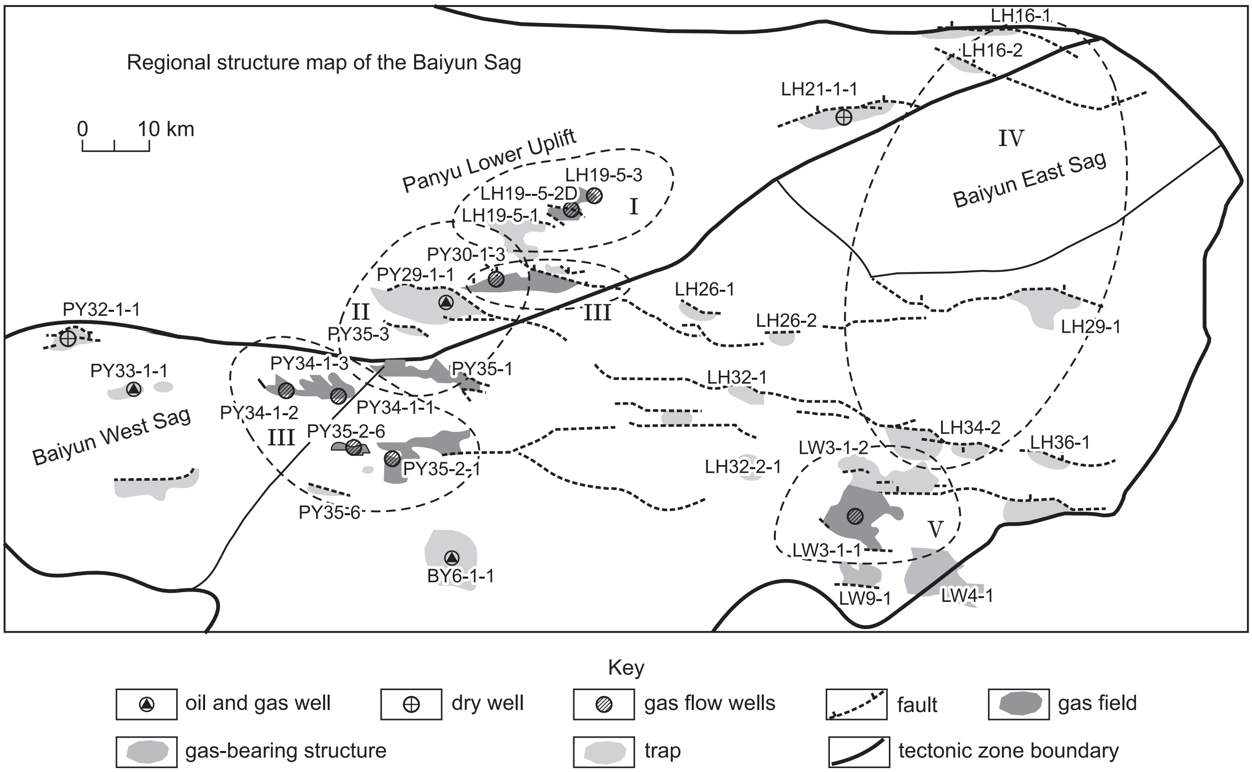


Fig. 13. Surface distribution of oil sources in the Baiyun Sag.

Note: I: organic matter (OM) derived from the Enping Fm, primarily; II: OM derived from the Enping and Wenchang Fms; III: OM derived from the Wenchang Fm, primarily; IV: OM derived from the Enping and Zhuhai Fms; IV: OM derived from the Enping, Wenchang, and Zhuhai Fms.

tures to the reservoirs in well PY30-1-2A. However, no large fault cuts across the Wenchang Fm at well PY30-1-3 (He et al., 2012), which is adjacent to well PY30-1-2A, where the Enping Fm is the primary source bed. To determine the relationship between oil source and geological conditions in the Baiyun Sag, future studies must combine geochemistry with tectonic movement.

CONCLUSIONS

The biological source of crude oil in the Baiyun Sag is terrigenous higher plants in a lacustrine depositional environment in oxidizing conditions, with the degree of terrigenous input in the northern sag greater than that in the eastern sag. Crude oils are mature to highly mature, and the maturity of crude oil in the northern sag is greater than that in the eastern sag.

The Enping Fm is the primary hydrocarbon source bed in the Baiyun Sag. The reservoirs in the northern area of Panyu Lower Uplift have hydrocarbon contributions from the Wenchang Fm, while reservoirs in the eastern area of the Liuhua-Liwan structure have hydrocarbon contributions from the Zhuhai Fm. Crude oils in the LH19-5 structure in the northern sag are from the source bed in the Enping Fm; oils in the PY34-1 and PY35-2 structures are from the Wenchang Fm, and oils in the PY35-1 structure and well PY30-1-3 and LH26-1-1 are of a mixed source from the Enping and Wenchang Fms. In the eastern sag, in the LH16-2, LH29-1, and LH34-2 structures, crude oils are mixed source oils from the Enping and Zhuhai Fms; oil in the LW3-1 structure is also of mixed source from the Enping, Wenchang, and Zhuhai Fms.

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